CHEMICAL AND BIOLOGICAL INVESTIGATIONS OF SOME CONSTITUENTS OF TECHNICAL CHLORDAN

BY

RALPH BURTON MARCH

A.B., University of Illinois, 1941

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

Technical Chlordan (recorded February 27, 1947 by the Commission of Patents as the compound containing not less than 60% 2,3,4,5,6,7,8,8-octachloro-4,7-methano-3a,4,7,7a-tetrahydroindane and 40% related active compounds) is a dense, viscous, dark amber to brown-colored liquid with a terpene-like odor. Kearns et al (1945) first reported and discussed the physical characteristics and insecticidal activity of this material. They suggested that it was possibly a mixture of isomers. Bruson and Riener (1945) reported that the hydration of dicylopentadiene with aqueous sulfuric acid yielded an unsaturated, secondary monohydric alcohol having a different ring system than the original diene. Bartlett and Schneider (1946) presented evidence that this acid-catalyzed hydration involved a normal Wagner-Meerwein rearrangement to yield the *exo*-isomer. It was thus proposed that Technical Chlordan might consits of *endo*- and *exo*-isomers of $C_{10}H_6Cl_8$ and related compounds. Attempts at the separation of such isomers by distillation and solubility methods were unsuccessful. The recent and wide application of chromatographic adsorbtion analysis to the resolution of mixtures of organic compounds suggested that this method be investigated.

Methods

Chromatographic Adsorbtion Analysis

Five gm. of Technical Chlordan in 10 ml. of medium boiling petroleum ether were adsorbed on a 19 x 300 mm. column of Merck anhydrous aluminum oxide and the flowing chromatogram was developed with the same solvent. The

percolate was arbitrarily collected in 10 ml. fractions since it was not possible to follow the chromatogram by physical or chemical means. The column was finally eluted with acetone and the various solute fractions were recovered upon evaporation of the solvent.

Test Insect

The adult female of the large milkweed bug, *Oncopeltus facsiatus* (DALLAS), was reared in sufficient numbers for test purposes according to the method as described by Worthley (1943).

Biological Evaluation

Test lots of 100 bugs each were used for the determination of time-mortality data at various dosages. The bugs were individually treated by the topical application of a calculated dose of toxicant in a measured drop of solvent, approximately 1.00 $mm.^3$ of dioxane. This application was accomplished by means of a hypodermic needle and syringe mounted on a wooden block and coupled to a hand-driven micrometer. The bugs were held for observation in Kerr pint jars provided with food and water and mortalities were determined at 24 ± 1 hr. intervals over a 144 hr. period following treatment.

Results

Adsorbtion Analysis

Ten adsorptions, each of 5 gm. Technical Chlordan (Adsorbtion A), were initially accomplished. Physically and biologically similar fractions from these adsorbtions were combined and readsorbed (Adsorbtions B-G). Again selected solute fractions were combined and readsorbed (Adsorbtions H-L). The mean solute fractions from this second series of readsorbtions were separately combined and then decolorized, recrystallized and or filtered to yield the five final constituents.

Chemical and Infrared Analyses

Constituent I

White crystalline solid, m.p. 154°C - decomposes
Analysis. Calculated for $C_{10}H_6Cl_6$: C,35.44; H,1.79; Cl,62.77.
Found: C,35.10; H,1.88; Cl,62.99.

Constituent II

White crystalline solid, m.p. 92.0-93.0°C
Analysis. Calculated for $C_{10}H_5Cl_7$: C,32.17; H,1.35; Cl,66.48. Found: C,32.36; H,1.70; Cl,66.22.

Constituent III

Colorless to faintly yellow viscous liquid, N 20/d 1.5804
Analysis. Found: C,31.53; H,1.76; Cl,66.26.

Constituent IV

White crystalline solid, m.p. 97.5-99.0°C
Analysis. Calculated for $C_{10}H_6Cl_8$: C,29.31; H,1.48; Cl,69.16. Found: C,29.39; H,1.75; Cl,69.16.

Constituent V

Colorless to faintly yellow viscous liquid, N 20/d 1.5750
Analysis. Found: C,31.68; H,1.98; Cl,65.72.

Infrared absorbtion spectra from 4000 - 650 $cm.^{-1}$ were determined for the five constituents. Comparison of the spectra shows that constituents I, II and IV are distinctly different compounds. The spectra of constituents III and V contain all the strong bands present in the spectrum of constituent IV plus many additional and individually distinct bands which are different from those of constituents I and II.

Biological Evaluation

Critical dosage-mortality curves for 96 hrs. following treatment were determined according to Bliss (1935) and Finney (1947) for Technical Chlordan and constituents II - V. Constituent I required such high dosages that comparable data were impractical. The LD50 values and their standard

deviations as obtained from the curves are as follows: Technical Chlordan 11.5 ± 0.2 microgm. per bug, constituent I > 75.8, constituent II 2.5 ± 0.1, constituent III 18.7 ± 0.6, constituent IV 37.1 ± 1.1 and constituent V 5.4 ± 0.1.

Discussion And Conclusions

Adsorbtion characteristics, physical constants and chemical and infared analyses provide evidence that the five constituents obtained are as follows:

Constituent I

4,5,6,7,8,8-hexachloro-4,7-methano-3a,4,7,7a-tetrahydroindene

Constituent II

1 or 3a,4,5,6,7,8,8-heptachloro-4,7-methano-3a,4,7,7a-tetrahydroindene

Constituent III

Mixture of constituent IV and unidentified component(s)

Constituent IV

2, 3, 4, 5, 6, 7,8,8-octachloro-4,7-methano-3a,4,7,7a-tetrahydroindane

Constituent V

Mixture of constituent IV and unidentified component(s)

It is not possible to say that one constituent is an isomeric form of another, or even less that a constituent is a specific isomer.

The ranges in the LD50 values for 96 hrs. following treatment are as follows: Technical Chlorodan 11.1 - 12.0 microgm. per bug, constituent I not determined, constituent II 2.4 - 2.6, constituent III 17.4 - 20.1, constituent 1V 34.6 - 40.0 and constituent V 5.2 - 5.6.

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VITA

Ralph Burton March was born August 5, 1919 in Oshkosh, Wisconsin, the son of Albert Harold and Vanita Siewert March. He completed his grammar school education at Longfellow School in June, 1933 and his high school education at Oskosh High School in June, 1937. In September, 1938 he transferred to the University of Illinois, Urbana, Illinois. In June, 1941 he was graduated from the University of Illinois with highest honors, receiving a Bachelor of Arts degree in Entomology. He continued his education at the University of Illinois in September, 1941 being awarded a first year graduate scholarship. In June, 1942 his education was interrupted when he was called to active duty as a Second Lieutenant in the Chemical Warfare Service. He served in varying capacities as Chemical Officer with the Army Air Forces until June, 1946 when he was released in the grade of Major. He re-entered the University of Illinois in June, 1946 and received a Master of Arts degree in Entomology in September, 1946. He continued his graduate studies in Entomology at the University of Illinois, being granted a third year graduate fellowship during the school year 1947-1948.

He was married to Robinetta Tompkin in San Francisco, California, December 26, 1942.

He is a member of Phi Beta Kappa, Phi Kappa Phi, Phi Sigma and an associate member of Sigma Xi. He belongs to the American Association of Economic Entomologists and the American Chemical Society.

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